Equilibrium Dynamics in an Entangled Polymer Blend

The dynamics of compositional fluctuations in a miscible, entangled homopolymer blend of poly(ethylene oxide) and poly(methyl methacrylate) were studied on length scales smaller than the polymer radii of gyration and for times comparable to the polymers' disentanglement time. The measured relaxation rates are consistent with predictions of the reptation model, as expressed via the dynamic random-phase approximation. Moreover, the observed mode amplitudes allow for an estimate of the entanglement length in the blend.

The emerging technique of x-ray photon correlation spectroscopy (XPCS) has recently been shown capable of studying the slow dynamics of colloidal systems at small length scales [1]. Applying XPCS to polymer blends is more challenging than applying it to colloids because of the smaller scattering cross section in blends. In this report, however, we present an XPCS study of dynamics in a homogeneous, binary blend of monodisperse, highly entangled chains of poly(ethylene oxide) (PEO) and poly(methyl methacrylate) (PMMA), investigating for the first time the nondiffusive relaxation of compositional fluctuations on length scales smaller than the extent of individual polymer coils and on time scales encompassing the disentanglement time.

Our methods for carrying out XPCS experiments are thoroughly described in Ref. 2. In brief, the dynamical properties of the blend were characterized via intensity autocorrelation of sequential two-dimensional scattering patterns, each obtained in a 5 s exposure of a CCD detector. The advantages of such a scheme for characterizing the dynamics of slow and glassy materials and for improving signal to noise have been emphasized previously [3–5]. The normalized intensity time-autocorrelation function, $g_2(Q,t)$, is related to the normalized intermediate scattering function (ISF). Typical blend autocorrelation functions, averaged over a small range in Q

and extending from 5.0 to 1500 s, were measured at three different mean wave vectors. To model these data, we have chosen an exponential ISF, which provides a good description of the measurements and enables us to determine the characteristic decay rate (Γ).

The fitted relaxation rates (Γ) at 70°C are plotted in Fig. 1 versus Q^2R^2. The most striking feature of Fig. 1 is that Γ varies only weakly with Q^2R^2—in marked contrast to a variation with at least Q^3 that would occur in this wave-vector range in the absence of entanglements [6]. Overall, the data are consistent with a crossover from an approximately Q^2 variation at smaller wave vectors to a constant at larger wave vectors.
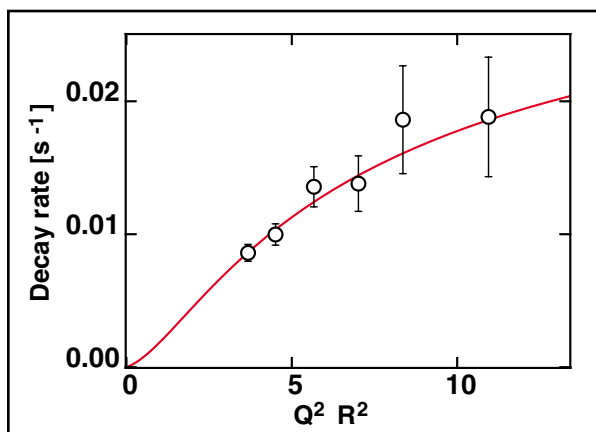

FIG. 1. Relaxation rates at 70°C versus Q^2R^2. The solid curve corresponds to the model described in the text.

In developing a model to describe the ISF of a polymer blend at time scales comparable to the disentanglement time, we assume it to be proportional to the normalized ISF due to reptation and the concentration fluctuation inside the tube to be an exponential factor dependent on d, the entanglement distance. Using complementary information from various other measurements [7], the disentanglement time was found to be 19.9 ± 0.9 s for the PMMA component and 44.2 ± 2.0 s for the PEO component. The expectation of this model is borne out in Fig. 1, where the solid line shows the result of the fit with the above relaxation times. This constitutes the principal result of this investigation. Also the analysis of the dependence of the apparent contrast with Q has allowed us to deduce the entanglement distance in the blend to be d = 7.8 ± 3.4 nm.

In summary, we have performed, for the first time, intensity fluctuation spectroscopy on an entangled polymer blend for wave vectors corresponding to the nondiffusive regime of the equilibrium compositional fluctuations. We find that the wave-vector dependence of the measured relaxation rates is consistent with the predictions of the reptation model. The reptation model also hypothesizes a link between the wave-vector dependence of the reptative mode amplitude and the entanglement distance. On this basis, we are able to estimate the mean entanglement length for our blend, finding a value that is comparable to the entanglement lengths of the component homopolymers. The relaxation rates presented in this work vary weakly with Q^2R^2, tending towards a constant relaxation rate at the largest wave vectors studied. This result is consistent with the predictions of the classical reptation model. Furthermore, the wave-vector dependence of the apparent contrast, interpreted within the framework of the reptation model, yields an entanglement length similar to that of the blend components.

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